Electronic Structure and Bonding Configuration of the $H$-Phases Ti$_2$MC and Ti$_2$MN ($M = \text{Al, Ga, In}$)


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Abstract—The electronic structure of the $H$-phases Ti$_2$MC and Ti$_2$MN ($M = \text{Al, Ga, In}$) is calculated by the self-consistent linearized muffin-tin-orbital method in the atomic-sphere approximation and the MO LCAO method using RMH parametrization. The band structure and bonding configuration of the $H$-phases are compared with those of other Ti–M–C and Ti–M–N phases.

Among the ternary phases existing in Ti–M–C and Ti–M–N systems ($M = \text{Group III and IV nontransition metals}$), there are hexagonal carbides and nitrides of stoichiometry Ti$_2$MC (Ti$_2$MN), called $H$-phases [1, 2]. In recent years, these phases have attracted a great deal of attention as potential materials for engineering applications [3, 4]. However, their electronic structure and bonding configuration have yet to be studied fully.

In this paper, we report the results of quantum-chemical calculations of the electronic structure and bonding parameters of Ti$_2$MC and Ti$_2$MN ($M = \text{Al, Ga, In}$).

The energy-band structure and density of states (DOS) were calculated by the self-consistent linearized muffin-tin-orbital (LMTO) method in the atomic-sphere approximation (ASA) [5]. Pair overlapping integrals were evaluated in a cluster approach using the MO LCAO method and Hückel’s parametrization [6].

The $H$-phases have a Cr$_2$AIN-type structure (sp. gr. $P6_3/mmc-D_{6h}^4, Z = 2$). The basic structural component is an octahedron of six Ti atoms, with a C or N atom residing in the center. Each octahedron shares six edges with neighboring octahedra. Goldschmidt [2] suggested that the Cr$_2$AIN structure can be regarded as a hexagonal analog of the cubic perovskite structure.

The structural basis of the Ti$_2$MC and Ti$_2$MN phases is shown in Fig. 1, and the unit-cell parameters are listed in Table 1.

The energy-band and DOS results for the $H$-phases under consideration are displayed in Figs. 2 and 3, respectively. As an example, consider the energy-band structure of Ti$_2$AlC (Fig. 2a). The two lowest, quasi-core bands consist of C 2s states and disperse insignificantly. They are separated by a gap from the manifold made up of eight valence bands derived from C 2p, Al 3s, and Al 3p states, with an admixture of outer Ti s, p, and d orbitals. At still higher energies, there is a fairly dense manifold consisting primarily of Ti and Al states. The bands located just at the Fermi level and intersecting $E_F$ include a sizeable contribution from antibonding C states. The band structure of the nitride phase Ti$_2$AlN is similar to that of the carbide analog: the lowest (quasi-atomic) states N 2s are located at $\approx 14$ eV and are separated by a gap from the N(2p)–Al(3s, 3p)–Ti(3d, 4s, 4p) manifold. These bands have a more atomic character. The broadening of this manifold in comparison with Ti$_2$AlC reflects the larger energy separation between the N 2p and Al s, p levels in comparison with the C 2p and Al s, p levels (Fig. 2).

In both Ti$_2$AlC $\rightarrow$ Ti$_2$GaC $\rightarrow$ Ti$_2$InC and Ti$_2$AlN $\rightarrow$ Ti$_2$GaN $\rightarrow$ Ti$_2$InN series, we find considerable changes in the structure of the $p$–$d$ band (Fig. 2), as clearly seen in DOS results (Fig. 3). In

![Fig. 1. Structural basis of the Ti$_2$MC and Ti$_2$MN (M = Al, Ga, In) phases.](image-url)
going from Al to In, the states of the nontransition metal become more localized, giving rise to DOS peaks near the bottom of the $p-d$ band (Fig. 3, Ti$_2$InC, Ti$_2$InN).

An important feature of all the $H$-phases is that the Fermi level is located in a DOS minimum (or at a small peak) between bonding and antibonding bands and, accordingly, the Fermi-level DOS $N(E_F)$ is relatively low (Table 2), which determines the thermodynamic stability of the $H$-phases.

Note that the electronic structure of the $H$-phases differs from that of cubic antiperovskite phases (Ti$_3$AlC, Ti$_3$GaC, and others [8]), in which the bonding and antibonding bands are separated by an extended plateau with a low density of nonbonding states and, for this reason, the concentration of valence electrons can vary widely, without destabilizing the electronic structure [8], which accounts for the broad stoichiometry ranges of the antiperovskite phases [2]. The present calculations suggest that, in the $H$-phases, changes in the concentration of valence electrons will be accompanied